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METASTABLE MIXED CRYSTALS WITH QUARTZ STRUCTURE
WITH THE OXIDE SYSTEM $Li_2O-MgO-ZnO-Al_2O_3-SiO_2$

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16. Abstract   The pseudoquaternary system $LiAlO_2-MgAl_2O_4-ZnAl_2O_4-SiO_2$ is studied. The concentrations of the four components in glasses which, upon crystallization, yield metastable mixed crystals with quartz structure are determined. Crystallization is carried out at temperatures between 800 and 1000°C. The glasses contain 2% TiO_2 and 2% ZrO_2 by weight as nucleating agents. The thermal expansion coefficients and hexagonal lattice constants of crystals prepared in this manner are measured as functions of the composition of the glass from which they crystallized. The effects of the various components on crystallization, expansion properties, and lattice constants are analyzed.

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METASTABLE MIXED CRYSTALS WITH QUARTZ STRUCTURE WITH THE OXIDE SYSTEM $Li_2O-MgO-ZnO-Al_2O_3-SiO_2$

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Corresponding to the substitution possibilities $Si^{4+} \rightleftharpoons Li^{+}$, /385* Al^{3+}; $2Si^{4+} \rightleftharpoons Mg^{2+}$, $2Al^{3+}$; $2Si^{4+} \rightleftharpoons Zn^{2+}$, $2Al^{3+}$ within the quartz structure, the pseudoquaternary system $LiAlO_2-MgAl_2O_4-ZnAl_2O_4-SiO_2$ was selected. Within this concentration range, the existence region of metastable mixed crystals with quartz structure is determined, if they are crystallized from powdered glasses containing (in wt-%) 2 TiO_2 and 2 ZrO_2 as nucleating agents for a period of 22 hours and at temperatures between 800 and 1000°C.

The coefficients of thermal expansion of glasses crystallized in this manner in the existence region of metastable mixed crystals with quartz structure in the given system were measured.

The hexagonal lattice constants of the mixed crystals are determined from x-ray diffractometer photographs with the aid of indexing of the x-ray reflections as in Roy [29]; their dependence on glass compositions from which the mixed phases crystallize is discussed.

1. Statement of the Problem

Recently, crystalline phases distinguished by extremely low coefficients of thermal expansion have gained increasing importance for the development of glass-ceramic materials with high resistance to temperature changes. In this regard, the compounds eukryptite and spodumene and the mixed crystals of these two phases with SiO_2 in the ternary oxide system $Li_2O-Al_2O_3-SiO_2$

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*Numbers in the margin indicate pagination in the foreign text.

are particularly interesting. Fundamental research on phase
equilibria, mixed-crystal formation, expansion properties, and
the structure of crystalline phases as well as the crystalliza-
tion products of glasses with and without nucleating agents in
the oxide system $Li_2O-Al_2O_3-SiO_2$ have been made by Hatch [1],
Roy and Osborn [2], Roy, Roy, and Osborn [3], Skinner and Evans
[4], Saalfeld [5], Smoke [6, 7], Henglein [8], Krishna Murthy
and Kirby [9], Eppler [10], Kondratev [11], Alekseev and
Zasolotskaya [12], Prokopowicz and Hummel [13].

References on the use of lithium aluminum silicates as
crystalline phases for the development of glass-ceramic materials
with high resistance to temperature changes are found in McMillan
[14], Sack [15], Sack and Scheidler [16], Baum [17], Williams   /386
and Carrier [18], Bokin et al. [19], Moriya et al. [20], Sakka
and Tashiro [21], Min Syu-kwei and Ying Bao-chung [22], Shaver
[23], Stookey [24], Hinz and Kunth [25], Stevels [26], and
Tashiro [27, 28].

This incomplete list of works -- there is an extensive patent
literature in this area -- ought to indicate the importance
attached to the development of glass-ceramics, particularly the
basic system $Li_2O-Al_2O_3-SiO_2$.

In the present work, the author deals with mixed crystals
of the type designated Silica O by Roy [29]. Such mixed crystals
are obtained from glasses of the oxide system $Li_2O-Al_2O_3-SiO_2$ with
compositions which lie on or near the pseudobinary join $Li_2O \cdot$
$Al_2O_3 \cdot 2SiO_2-SiO_2$, metastable through crystallization at tempera-
tures about 800°C [11]. Schreyer and Schairer [30] found that
mixed crystals of the same type can be obtained by crystalliza-
tion of glasses of the pseudobinary system $MgAl_2O_4-SiO_2$. Beall
et al. [31] described the possibility of injecting Zn^{2+} cations

2

into the h-quartz lattice, although only in h-quartz lattices of mixed crystals of the pseudobinary joins $LiAlO_2$-SiO_2 or $MgAl_2O_4$-SiO_2. The authors found no mixed crystals with h-quartz structure in the system $ZnAl_2O_4$-SiO_2.

With regard to ease of melting and working, economic utility of the glasses, and the possibility of converting them to the glass-crystalline state with the aid of suitable nucleating agents, and experimentally determined tempering programs, the polynary oxide system Li_2O-MgO-ZnO-Al_2O_3-SiO_2 with TiO_2 and ZrO_2 as nucleating agents is particularly interesting.

By controlled crystallization of glasses of this oxide system, both transparent and opaque glass ceramic materials can be obtained [16].

The present work, therefore, is intended to help answer the following questions:

1. Within what ranges of concentration and under what crystallization conditions can metastable mixed crystals with quartz structure be obtained from glasses of the system Li_2O-MgO-ZnO-Al_2O_3-SiO_2?

2. What is the influence of the replacement of Li^+ by Mg^{2+} and Zn^{2+} in the mixed crystals on the expansion properties?

This last question has become especially crucial since Sack and Scheidler, in the course of systematic development work on glass ceramics with compositions of the given polynary system, discovered that the replacement of Mg^{2+} by Zn^{2+} in the starting glasses resulted in masses with very low coefficients of expansion after the transformation into the glass-crystalline state.

3

2. Methods

2.1. Composition of the Specimens

Metastable mixed crystals with quartz structure of the system $LiAlO_2-SiO_2$ are, in the terminology of Buerger [32], so-called "stuffed derivatives" of the h-quartz. In the formation of mixed crystals, Si^{4+} is replaced by Li^+Al^{3+}, where Al^{3+} occupies the lattice positions of Si^{4+}, while Li^+ situates in the holes of the quartz structure.

Mixed crystals with quartz structure produced by the substitutions $2Si^{4+} \rightleftarrows Mg^{2+}\ 2Al^{3+}$ and $2Si^{4+} \rightleftarrows Zn^{2+}\ 2Al^{3+}$ are also such stuffed derivatives. From the oxide system $Li_2O-MgO-ZnO-Al_2O_3-SiO_2$, the pseudoquaternary system $SiO_2-LiAlO_2-MgAl_2O_4-ZnAl_2O_4$ was selected, from which the substitution possibilities of the Si^{4+} in the quartz structure can be directly recognized. Within the pseudoquaternary system, the pseudobinary joins $LiAlO_2-SiO_2$ and $ZnAl_2O_3-SiO_2$ as well as the pseudoternary systems $LiAlO_2-MgAl_2O_4-SiO_2$; $LiAlO_2-ZnAl_2O_4-SiO_2$; and $MgAl_2O_4-ZnAl_2O_4-SiO_2$ were successively studied for existence regions of metastable mixed crystals with quartz structure. Finally, two other joins with 60 and 70% SiO_2 by weight were placed through the entire pseudoquaternary system, in order to see whether stuffed derivatives of quartz turned up in these regions as well containing Li^+, Mg^{2+}, and Zn^{2+} in adjacent lattice holes.

The join $LiAlO_2-SiO_2$ was once again studied, since the literature contained conflicting figures on the region of metastable crystal formation (see Section 3.1.1). We adopted the figures of Schrayer and Schairer [30] with reference to the metastable mixed crystals with quartz structure in the system $MgAl_2O_4-SiO_2$.

The compositions of the specimens studied were calculated in percentages by weight for the four components SiO_2, $LiAlO_2$, $MgAl_2O_4$, and $ZnAl_2O_4$. However, in order to be able to give in meaningful form the lattice constants of the resulting metastable mixed crystals with quartz structure as functions of the composition of the starting glasses, the percentages by weight must be converted into molar percentages, where it must be kept in mind that the molecular weights for this conversion must be those of formula units with the same number of oxygen atoms in each case (the system Si_2O_4-$Li_2Al_2O_4$-$MgAl_2O_4$-$ZnAl_2O_4$). All investigated glasses received 2% TiO_2 and 2% ZrO_2 by weight as nucleating agents.

This nucleating agent combination was chosen on the basis of the experience of Sack and Scheidler [16], who found that TiO_2 and ZrO_2 were particularly effective when added as nucleating agents for controlled crystallization of metastable quartz mixed crystals of glasses of the basic system Li_2O-Al_2O_3-SiO_2.

2.2. Preparation of the Specimens

Glasses of the desired composition were prepared in 100-g batches: SiO_2 (Sipur), Li_2CO_3 p.a., Al_2O_3 p.a., MgO p.a., and ZnO p.a. were intensively homogenized for about 30 minutes in a conical mill. Depending on composition, the mixtures were melted 30 minutes at 1550 to 1620°C in Pt crucibles, quenched in water, homogenized again, and finally held again at temperatures between 1550 and 1620° for 1 hour. The glasses were then quenched in air, and examined microscopically for any resulting crystallization. Only "clean" glasses were pulverized, pressed into bars, and in this form tempered for 22 hours at temperatures between 800 and 1050°C. The most favorable temperature for the /387 crystallization of metastable mixed crystals with quartz structure with a tempering period of 22 hours varied between 800 and 1050°C as a function of the composition of the specimens.

2.3. Methods of Investigation

An x-ray diffractometer device (Siemens) was employed for the x-ray investigation of the tempered specimens with CuK α-radiation. Powders were prepared by the known methods. Si-powder was used as a calibrating substance for reproducible depiction of the d-values of the x-ray reflections.

In order to be able to follow the formation of mixed crystals in the investigated concentration range, the lattice constants of the metastable mixed crystals were determined as functions of the composition of the glasses from which they had crystallized. To calculate the hexagonal lattice constants a_{hex} and c_{hex} of the quartz lattice of the mixed crystals, the indexing of Roy [29] was used; here a_{hex} was found from the reflections 100 and 200, c_{hex} from the reflections 112 and 211. The accuracy obtained in this way in the determination of the lattice constants (± 0.005 Å) appeared sufficient, since with the chosen method of preparation, the composition of the resulting mixed crystals cannot be given with absolute assurance, since even small quantities of any remaining glass phase still present will cause the composition of the mixed crystals to deviate noticeably from that of the weighed sample. A tempering period of 22 hours was found by x-ray crystallography to be particularly favorable; both with respect to the smallest possible residual glass phase (the lattice constants of mixed crystals varied in tempered samples which had been treated for 12 hours or less, while longer tempering periods had no effect on the lattice parameters), and with respect to the smallest degree of decomposition of the metastable mixed crystals (at the chosen crystallization temperatures, the mixed crystals did not begin to decompose until tempered for more than 30 hours). It remains to observe that the tempering time of 22 hours prescribed for all the specimens studied requires a most favorable

crystallization temperature which is a function of the composition, and which will be further discussed along with the results of the investigations into the individual subsystems.

The semiquantitative statements which can be made regarding the dependence of the lattice constants of the mixed crystals on the composition of the glasses from which they crystallized are nevertheless sufficient to clarify the question of mixed crystal formation in the entire system. In the graphic depictions of these relationships, the mol-% composition is always given for the weighed sample.

For expansion measurements in a silica-glass dilatometer, expansion rods were cut from the tempered bars, and the α-values were measured between 20 and 300°C. As far as the graphs of the α-values of the specimens as functions of composition, it should be kept in mind that it was not the composition of the mixed crystals but, correctly, the composition of the crystallized melts (based on the weighed sample) at the given tempering conditions which was plotted on the horizontal axis. The crystallized melts can still contain residues of glass phase or small amounts of other crystalline phases (e.g. gahnite at incipient decomposition of the metastable mixed crystals).

3. Results

3.1. Metastable Mixed Crystals with Quartz Structure in the System $LiAlO_2-SiO_2$

According to Roy [29], there is in this system a continuous series of metastable mixed crystals with h-quartz-type structure between $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ and SiO_2. On the other hand, Alekseev [12] found the same metastable mixed crystals in crystallization of glasses of the pseudobinary join $LiAlO_2-SiO_2$ with 5 mol-% TiO_2 as nucleating agents at crystallization temperatures of

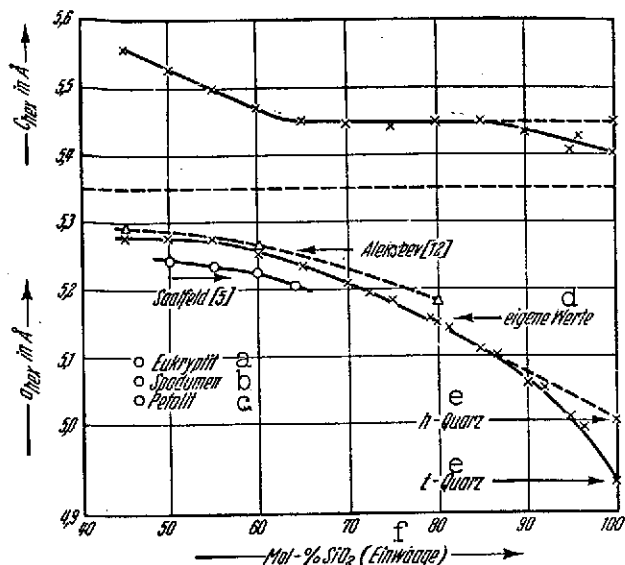830°C in the concentration range between 45 and 80 mol-% SiO_2 (cf. Fig. 1). Saalfeld [5] obtained mixed crystals with h-quartz structure in the concentration range $Li_2O \cdot Al_2O_3 \cdot 2SiO_2 - Li_2O \cdot Al_2O_3 \cdot 3.5SiO_2$ through reaction in the solid state at 1300°C. The mixed crystals synthesized in this manner did not, however, completely agree in structure with mixed crystals of the same composition obtained through crystallization of glasses at 800 to 900°C.

Fig. 1. Lattice constants of metastable mixed crystals with quartz structure in the system $LiAlO_2$-SiO_2.
Crystallization conditions: 22 hours, 900°C.

Key: a. Eukryptite
     b. Spodumene
     c. Petalite
     d. Our own values
     e. Quartz
     f. Weighed sample

The difference is in the cation ordering conditions. Kondratev [11] showed this by infrared-spectroscopic investigations using the example of h-eukryptite: While there were no Si-O-Al(IV) bands in h-eukryptite (crystallization temperature 1200°C), such bands are found for a crystalline phase of the same lattice type which crystallized at 830°C. In the first case, there is an ordering into SiO_4 and AlO_4 layers, while in the latter case, this ordering has not yet occurred. This fact also has an effect on the magnitudes of the lattice constants of the mixed crystals under consideration. (Fig. 1: the a_{hex} values of the mixed crystals according to Saalfeld [5] were lower than the values of Alekseev [12], which are roughly equal to our values.)

8

3.1.1. Dependence of Lattice Constants of Metastable Mixed Crystals with Quartz Structure on the Composition in the System $LiAlO_2-SiO_2$

The results of the studies on this system are summarized in Fig. 1. The samples were prepared and studied as described in Section 2.2. The crystallization temperature was 900°C. In agreement with Alekseev, a limit mixed crystal was found on the $LiAlO_2$-rich side of the system at the given crystallization conditions. Its composition in mol-% was 45 SiO_2 and 55 $LiAlO_2$. A specimen crystallized at 900°C (22 hours) of composition (in mol-%) 40 SiO_2 60 $LiAlO_2$ already contained x-ray-crystallographically detectable tetragonal $LiAlO_2$ in addition to metastable quartz-type mixed crystals. The lattice constants a and c of mixed crystals from glasses of composition (in mol-%) 45 SiO_2 55 $LiAlO_2$ and 40 SiO_2 60 $LiAlO_2$ were identical. On the SiO_2-rich side of the system, such mixed crystals were still obtained by crystallization of a glass of mol-% composition 95 SiO_2 5 $LiAlO_2$.

It should be recalled that every sample received 2% TiO_2 and 2% ZrO_2 by weight. The figures of Roy [29], according to which there were no mixing gaps worth mentioning on the high-SiO_2 side of the $LiAlO_2-SiO_2$ system with respect to the crystallization of metastable "Silica-O phases," were confirmed by our results.

The dependence of the lattice constants a_{hex} on the composition appears clear: The replacement of Si^{4+} cations ($r_{Si^{4+}}$ = 0.39 Å according to Goldschmidt) by the larger cations Al^{3+} ($r_{Al^{3+}}$ = 0.57 Å) and Li^+ (r_{Li^+} = 0.78 Å) stretches the quartz lattice in the direction of the a-axis. There is also stretching in the c-direction, but it is irregular. The increase of the value of c_{hex} on the high-$LiAlO_2$ side of the system is explained by increasing ordering of Al^{3+} and Si^{4+} cations in the lattice

9

positions of the quartz structure of the mixed crystals [33].
The behavior of both lattice constants in the range between 80
and 100 mol-% SiO_2 indicates that the structure of the meta-
stable mixed crystals under the given crystallization conditions
tends toward the t-quartz structure (the broken lines are extra-
polations of the c- and a-curves to the lattice constant values
for h-quartz). In the region of 80 to 100 mol-% SiO_2, both
lattice constant curves approach the a- and c-values of t-quartz.
In the x-ray diffraction pattern of mixed crystals obtained from
glasses of the concentration region under discussion at 900°C
(22 hours), the appearance of the 111 reflection, which is
characteristic for t-quartz, can actually be observed. In
addition, the intensity ratio of the 102 and 200 reflections
in this concentration range climbs rapidly to the value charac-
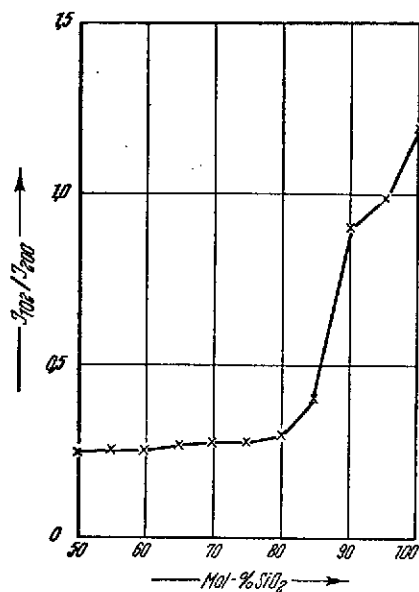teristic for the t-quartz structure (Fig. 2).

Fig. 2. Intensity ratios of the
x-ray reflections 102 and 200 of
mixed crystals in the system
$LiAlO_2$-SiO_2.

3.1.2. Remarks on the Nomen-clature of the Metastable Mixed Crystals Under Investigation

The results of the
x-ray crystallography
suggest that the structure
of metastable mixed crystals
obtained from glasses of
the $LiAlO_2$-SiO_2 system at
900°C increasingly resembles
t-quartz with increasing
SiO_2 content (room tempera-
ture, above 80 mol-% SiO_2).
If this is the case, the
physical properties of these
mixed phases must likewise

10

show a marked change above 80 mol-% SiO_2. For instance, the
slightly negative expansion characteristic of the h-quartz
structure must change suddenly into the strongly positive one
of the t-quartz structure. Figure 3 shows expansion curves of
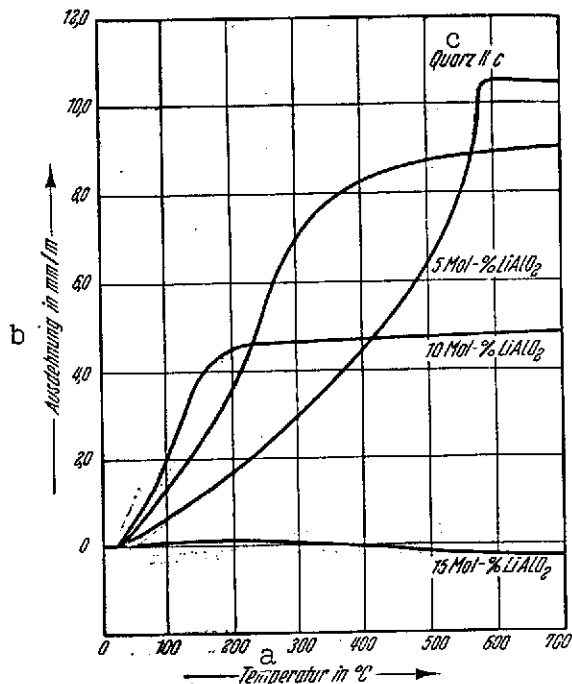a quartz crystal parallel to c in comparison with expansion
curves of three mixed
crystals with 5, 10 and 15
mol-% $LiAlO_2$, respectively,
between 20 and 700°C. The
large positive expansion
of t-quartz transposes to
the small negative one of
h-quartz at 573°C. The
injection of 5 mol-% $LiAlO_2$
is enough to depress the
transformation point by
about 100°, and spreads
it out over a wide tempera-
ture range. These phenomena
had already been described
by Keith and Tuttle [34]
and Hummel [35]. The
injection of 10 mol-% $LiAlO_2$
further depresses the trans- /389
formation point into the
vicinity of 200°C, until
the injection of 15 mol-%
$LiAlO_2$ finally pushes the

Fig. 3. Expansion behavior of
crystallized melts of the $LiAlO_2$-
SiO_2 system in comparison with
quartz.

Key: a. Temperature in °C
     b. Expansion in mm/m
     c. Quartz

transformation point below room temperature. These results and
those of the x-ray crystallography show clearly that the struc-
ture of the metastable mixed crystals with quartz structure in
the $LiAlO_2$-SiO_2 system at room temperature depends on the SiO_2
content, and that at least in the concentration range of 80 to
100 mol-% SiO_2, there is a phase transition h-quartz ⇄ t-quartz.

11

This could also be demonstrated for the mixed crystal 10 mol-% $LiAlO_2$, 90 mol-% SiO_2 with a heating-chamber attachment to the x-ray diffractometer. Roy [29] named the mixed crystals obtained from glasses of the $Li_2O \cdot Al_2O_3 \cdot 2SiO_2 - SiO_2$ system at temperatures of 900°C and below "Silica-O," primarily to indicate that the structure of the mixed crystals is not identical with the actual quartz structure, inasmuch as no high-low transformations or low-structures were observed in the metastable mixed crystals of this system. On the other hand, the present results seem to justify calling the mixed crystals under discussion metastable mixed crystals with quartz structure. Whether the mixed crystals exhibit h-quartz or t-quartz structure depends on the SiO_2 content.

3.1.3. Expansion Properties of Crystalline Melts of the $LiAlO_2$-SiO_2 System

Figure 4 shows the expansion behavior of crystallized melts of the $LiAlO_2$-SiO_2 system with 2% TiO_2 and 2% ZrO_2 by weight as nucleating agents between 20 and 300°C. The crystallization conditions were chosen to obtain the "most negative" expansion values, i.e. in the concentration range of 45 to 60% SiO_2 by weight, 22 hours and 1000°C; and between 60 and 92 SiO_2 by weight, 22 hours and 900°C. If a crystallization temperature of 900°C is chosen in the range 45 to 60% SiO_2 by weight as well, the products are crystallized melts whose α_{20-300} values are not less than $-10 \cdot 10^{-7}$/°C. Hahn and Behruzi [33] found that the lattice constant c_{hex} of metastable mixed crystals with quartz structure in this concentration range of the $LiAlO_2$-SiO_2 system, particularly with the eukryptite composition, is a function of the crystallization temperature, a phenomenon which is attributed to the ordering processes in the mixed crystal lattice. At 1000°C, Hahn and Behruzi obtained the largest value for c_{hex}. If these results are compared with the observation that the expansion
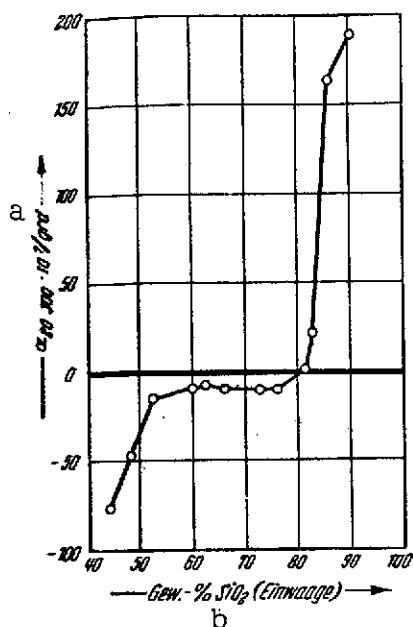
12

Fig. 4. Expansion behavior of crystallized melts of the SiO_2-$LiAlO_2$ system. Crystallization conditions: 22 hours, 45 to 60% SiO_2 by weight: 1000°C. 60 to 92% SiO_2 by weight: 900°C.

Key: a. Degree
b. % SiO_2 by weight (weighed sample)

values of crystallized melts with the composition of eukryptite (crystallization temperature 900°C) are substantially higher ($\alpha \sim -10 \cdot 10^{-7}/°C$) than the α-values of crystallized melts of the same composition (crystallization temperature 1000°C) with values around $-70 \cdot 10^{-7}/°C$, it becomes clear that the magnitude of the lattice constant c_{hex} of metastable mixed crystals constitutes a standard for the expansion values to be expected for the mixed phases. The larger c_{hex}, the more pronounced the anisotropy of the expansion will be. This is the well-known explanation of the negative expansion values of h-eukryptite (Gillery and Bush [36] give the following expansion values for h-eukryptite: $\alpha_{||c} = -176 \cdot 10^{-7}/°C$, $\alpha_{||a} = 87 \cdot 10^{-7}/°C$; mean value: $\alpha = -90 \cdot 10^{-7}/°C$).

Negative expansion values of crystallized melts in the $LiAlO_2$-SiO_2 system were observed up to a SiO_2 content of about 80% SiO_2 by weight. Crystallized melts with higher SiO_2 levels suddenly took on large positive α-values between 20 and 300°C. This result has already been shown in different form in Fig. 3. The large positive expansions between 20 and 300°C of crystallized melts of the system $LiAlO_2$-SiO_2 with SiO_2 concentrations between 80 and 100% by weight can be attributed to the t-quartz nature of the structure of the metastable mixed crystals crystallized under those conditions.

13

3.2. Metastable Mixed Crystals with Quartz Structure in the $ZnAl_2O_4$-SiO_2 System

Although Beall [31] points out that Zn^{2+} cations also can fill the holes of the h-quartz lattice, there are still no figures on lattice constants and expansion coefficients of metastable mixed crystals with quartz structure which can be <u>/390</u> obtained as crystallization products from glasses of the pseudo-binary system $ZnAl_2O_4$.

3.2.1. Lattice Constants of Metastable Mixed Crystals with Quartz Structure in the $ZnAl_2O_4$-SiO_2 System

In order to obtain from the glasses of this system (which, in addition to the two components $ZnAl_2O_4$ and SiO_2, also contain 2% TiO_2 and 2% ZrO_2 by weight) metastable mixed crystals with quartz structure as the only crystalline phase identifiable through x-ray crystallography as a result of tempering pulverized glass specimens for 22 hours, the crystallization temperatures must be increased from 800 to 1070°C as the SiO_2 content of the specimens increases. In each case, the metastable crystals were obtainable only at a crystallization temperature which was the lowest possible for a specific glass composition in this system. Figure 5 shows the results of the lattice constant determinations for such metastable mixed crystals in the $ZnAl_2O_4$-SiO_2 system under the given crystallization conditions. It turned out that replacing $2Si^{4+}$ by Zn^{2+}, $2Al^{3+}$ stretched the quartz lattice in the direction of the a-axis (comparable with the stretching of the quartz lattice with the substitution $Si^{4+} \rightleftarrows Li$, Al^{3+}). On the other hand, no dependence of the lattice constants c_{hex} on the composition of the mixed crystals was found. In all, the lattice volume is understandably increased by injecting into the quartz structure the cations Zn^{2+} ($r_{Zn^{2+}} = 0.83$ Å) and Al^{3+} ($r_{Al^{3+}} = 0.57$ Å) which are larger than Si^{4+}.
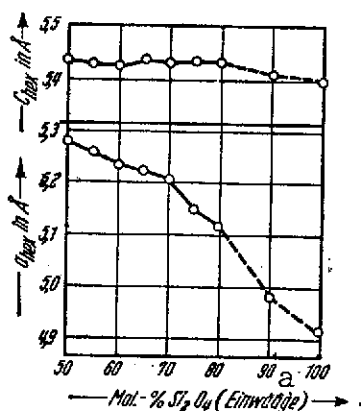
14

Fig. 5. Lattice constants of metastable mixed crystals with quartz structure in the SiO_2-$ZnAl_2O_4$ system. Crystallization conditions: 22 hours, 50-70 mol-% SiO_2: 800°C; 7085 mol-% SiO_2: 900°C; 85-90 mol-% SiO_2: 1070°C.

Key: a. Weighed sample

Mixed crystals with quartz structure as the only crystalline phase detectable by x-ray crystallography could be obtained in crystalline melts in the composition range 50 to 80 mol-% Si_2O_4. Gahnite always crystallized out of glasses with higher $ZnAl_2O_4$ concentrations, while small amounts of cristobalite were observed as a crystallization product in addition to the quartz mixed crystals when, under the given conditions, the SiO_2 content was greater than 80 mol-% Si_2O_4. Accordingly, it was expected that in this region the composition of the quartz mixed crystals differed markedly from the weighed sample (broken parts of the a_{hex} and c_{hex} curves in Fig. 5).

It was interesting to observe that the metastable quartz mixed crystals could not be obtained from compact glass specimens of the $ZnAl_2O_4$-SiO_2 at the chosen nucleating agent concentrations. In all experiments, the only crystal phase to crystallize out was gahnite. The devitrification temperatures of the compact glass specimens obviously lay outside of the metastability region of the quartz mixed phases in this system. Above the crystallization temperatures given in Fig. 5, the initially formed metastable mixed crystals began progressively to decompose into $ZnAl_2O_4$ and mixed crystals lower in spinel until almost pure quartz was present in addition to $ZnAl_2O_4$. The quartz converted to cristobalite so that after sufficiently long tempering periods,

gahnite and cristobalite were present as equilibrium phases above the temperatures given in Fig. 5.

3.2.2. The Expansion Properties of Crystallized Melts in the $ZnAl_2O_4$-SiO_2 System

The expansion behavior of crystallized melts of the $ZnAl_2O_4$-SiO_2 system, which contained the metastable mixed crystals under investigation as the principal product of devitrification, is depicted in Fig. 6 by α_{20-300} as a function of the composition of the crystallized melts. Negative expansions were observed in the c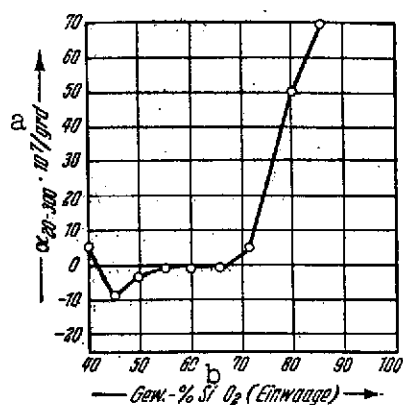oncentration region 45 to 68% SiO_2 by weight. The small positive value of α for the crystallized melt with 40% SiO_2 by weight can be attributed to the co-crystallization of gahnite. The rapidly rising expansion values of the crystallization products in the SiO_2-rich part of the system are due to cristobalite crystallizing out and due to an increasing low-temperature quartz nature of the structure of the high-SiO_2 mixed crystals of this system. The t-quartz structure of some high-SiO_2 mixed crystals above 80% SiO_2 by weight could again be clearly demonstrated by x-ray crystallography. Extremely low expansion values, such as those found in the system $LiAlO_2$-SiO_2 in the vicinity of the eukryptite composition, were not measured in the $ZnAl_2O_4$-SiO_2 system. This observation supports the

Fig. 6. Expansion behavior of crystallized melts of the SiO_2-$ZnAl_2O_4$ system. Crystallization conditions: 22 hours, 40-62% SiO_2: 800°C; 62-80% SiO_2: 900°C; 80-86% SiO_2: 1070°C (all % by weight).

Key: a. Degree
     b. % SiO_2 by weight
        (weighed sample)

16

hypothesis that a rise in the lattice constant c_{hex} of the h-quartz structure makes the expansions of the crystalline phases more negative. In the $LiAlO_2$-SiO_2 system, c_{hex} clearly increases with increasing $LiAlO_2$ content from the point 60 mol-% SiO_2, while the α-values of the crystal phases decrease. In the $ZnAl_2O_4$-SiO_2 system, c_{hex} remains roughly constant over the investigated composition range, and correspondingly, the measured α-values did not vary widely over the interval 45 to 68% by weight.

3.3. Expansion Properties of Crystallized Melts of the System $MgAl_2O_4$-SiO_2

Figure 7 shows lattice constants of metastable mixed crystals with quartz structure in the $MgAl_2O_4$-SiO_2 system according to Schreyer and Schairer [30]. It is striking that the insertion of Mg^{2+} (r_{Mg2+} = 0.78 Å) and Al^{3+} into the quartz lattice causes the lattice to contract in the c-direction while a_{hex} increases. On the expansion behavior of the mixed crystal phases in this system, the authors merely state that they [sic] are very low. For this reason, a specimen of composition (in wt-%) 50 $MgAl_2O_4$, 50 SiO_2 (+2TiO_2, +2ZrO_2) was melted, pulverized, and tempered for
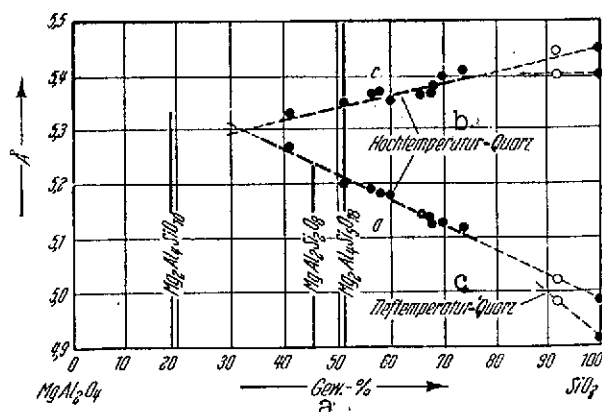

Fig. 7. Lattice constants of metastable mixed crystals with quartz structure in the system $MgAl_2O_4$-SiO_2 according to Schreyer and Schairer [30].

Key: a. % by weight
     b. High-temperature quartz
     c. Low-temperature quartz

22 hours at 900°C. The only crystal phase detectable by x-ray crystallography was a metastable mixed crystal with quartz structure. The expansion of these crystallized melts (α_{20-300} = = 42·10^{-7}/°C) was clearly higher than that of analogous samples

17

in the $LiAlO_2-SiO_2$ and $ZnAl_2O_4-SiO_2$ systems. This result fits with the idea that smaller values of the lattice constant c_{hex} imply less anisotropy in the expansion in the h-quartz structure of the metastable mixed crystals, and thus larger expansion values for the mixed phases (Table 1).

TABLE 1. LATTICE CONSTANTS c_{hex} AND EXPANSION α_{20-300} OF META-STABLE MIXED CRYSTALS.

Composition of the Sample in wt-%		Lattice Constant c_{hex} in Å	α_{20-300} in $10^{-7}/°C$
50 $LiAlO_2$	50 SiO_2	5.50	-50
50 $ZnAl_2O_4$	50 SiO_2	5.43	-3
50 $MgAl_2O_4$	50 SiO_2	5.34	+42

3.4. Metastable Mixed Crystals with Quartz Structure in the System $LiAlO_2-MgAl_2O_4-SiO_2$

The results of studies on samples of the pseudobinary joins $LiAlO_2-SiO_2$ and $MgAl_2O_4-SiO_2$ suggest that under suitable crystallization conditions, the pseudoternary system $LiAlO_2-MgAl_2O_4-SiO_2$ will exhibit mixed crystals with quartz structure of the general form $Li_{(2-2x)}Mg_xO \cdot Al_2O_3 \cdot ySiO_2$.

3.4.1. Lattice Constants of Metastable Mixed Crystals with Quartz Structure in the System $LiAlO_2-MgAl_2O_4-SiO_2$

The initial exploratory experiments on samples of this system yielded a limit of the existence region of the mixed phases to be investigated under the chosen crystallization conditions at about 45 to 50% SiO_2 by weight. Similar results were obtained for the systems $LiAlO_2-ZnAl_2O_4-SiO_2$ and $MgAl_2O_4-ZnAl_2O_4-SiO_2$, so that only the high-$SiO_2$ corners of the pseudoternary systems were investigated (from 50% SiO_2 by weight on up).

18

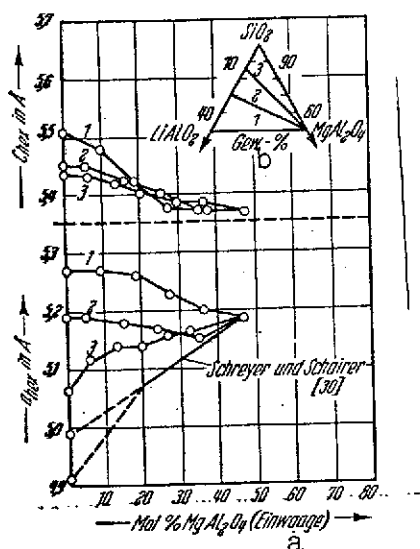Fig. 8. Lattice constants of metastable mixed crystals with quartz structure in the system SiO_2-$LiAlO_2$-$MgAl_2O_4$. Crystallization conditions: 22 hours, 900°C.

Key: a. Weighed sample
b. % by weight

Figure 8 shows the investigated region in the concentration triangle. Three pseudobinary joins were made through this region, and samples with the compositions shown in Fig. 8 were studied. Metastable mixed quartz crystals were found to be the only crystalline phase detectable by x-ray crystallography in samples tempered for 22 hours at 900°C. The more $MgAl_2O_4$ they contained, the faster the lattice constants c_{hex} of these mixed phases decreased. These results agree with those of Schreyer and Schairer [30]. The insertion of $MgAl_2O_4$ into the mixed crystals of the system $LiAlO_2$-SiO_2 causes the lattice constant a_{hex} to increase or decrease, depending on the $LiAlO_2$ content of the initial mixed crystals.

Looking at Join 3 in Fig. 8, it can be seen that a_{hex} is increasing. This is plausible since in this pseudobinary join, many smaller Si^{4+} are being replaced by larger Mg^{2+}, Al^{3+}, which stretches the lattice in the a-direction. On the other hand, looking at the case of Join 1 in Fig. 8, it is clear that there the insertion of $MgAl_2O_4$ causes a contraction in the a-direction. This finding can be explained as follows: Along Join 1, the SiO_2 content of the mixed crystals hardly changes at all, even in terms of mol-%, so that from left to right, there is a replacement $2Li^{+}\ 2Al^{3+} \rightleftarrows Mg^{2+}\ 2Al^{3+}$; i.e. the concentration of

19

larger cations in the vacancies of the quartz structure decreases with continuing insertion of $MgAl_2O_4$, since for each Mg^{2+} cation entering the lattice, two Li^+ cations must leave. The process obviously causes the contraction of the quartz lattice of these matastable mixed crystals in the direction of the a-axis.

3.4.2. Expansion Properties of Crystallized Melts of the System $LiAlO_2-MgAl_2O_4-SiO_2$

Figure 9 shows the expansion coefficients of crystallized melts tempered at 900°C for 22 hours. It is clear that the insertion of $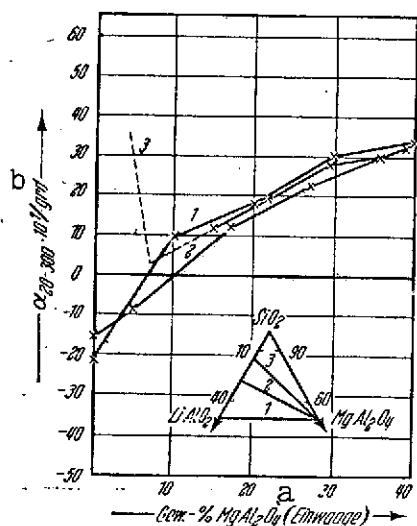MgAl_2O_4$ into the mixed crystals of the pseudobinary system $LiAlO_2-SiO_2$ makes the expansion coefficients of the resulting mixed crystals rise rapidly. Once again comparing the behavior of the lattice constants c_{hex} in Fig. 8 as the $MgAl_2O_4$ content /392 of the samples increases, the often mentioned relationship between the magnitude of the lattice constants c_{hex} and the expansion coefficients of the mixed crystals can be recognized: The steady drop in the values for c_{hex} in mixed phases with increasing $MgAl_2O_4$ content parallels a rise in their expansion coefficients. (Naturally, this holds only for mixed crystals with h-quartz structure.)

Fig. 9. Expansion properties of crystallized melts of the system $SiO_2-LiAlO_2-MgAl_2O_4$. Crystallization conditions: 22 hours, 900°C.

Key: a. % by weight $MgAl_2O_4$ (weighed sample)
b. Degree
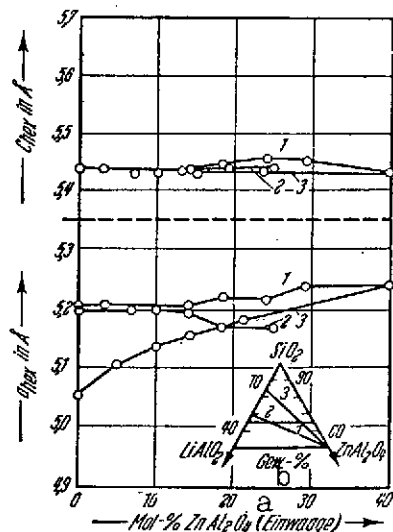
Fig. 10. Lattice constants of metastable mixed crystals with quartz structure in the system SiO_2-$LiAlO_2$-$ZnAl_2O_4$. Crystallization conditions: 22 hours, 900°C.

Key: a. Weighed sample
b. % by weight

3.5. Metastable Mixed Crystals with Quartz Structure in the System $LiAlO_2$-$ZnAl_2O_4$-SiO_2

As in the experiments in the $LiAlO_2$-$MgAl_2O_4$-SiO_2 system, we prove in the following that in the pseudoternary system $LiAlO_2$-$ZnAl_2O_4$-SiO_2 as well, metastable mixed crystals with quartz structure of the general form $Li_{(2-2x)}Zn_x \cdot O \cdot Al_2O_3 \cdot ySiO_2$ can be obtained under certain crystallization conditions from glasses which contain at least 50% SiO_2 by weight.

3.5.1. Lattice Constants of Metastable Quartz Mixed Crystals in the System $LiAlO_2$-$ZnAl_2O_4$-SiO_2

The position of the investigated pseudobinary join in the high-SiO_2 corner of this system and the dependence of the lattice constant values of the resulting mixed quartz crystals on the composition of the initial melts can be seen from Fig. 10. The crystallization conditions were 22 hours, 900°C. At this temperature, the mixed crystals (particularly the ones high in $ZnAl_2O_4$) showed the signs of an incipient breakdown. The first weak gahnite reflections could be seen in the x-ray diffraction patterns of the crystallization products in the high-$ZnAl_2O_4$ part of the concentration range investigated.

No clear changes in the lattice constants c_{hex} were observed as $ZnAl_2O_4$ was injected into the mixed quartz crystals of the system $LiAlO_2$-SiO_2. The dependence of the lattice constants

21

a_{hex} on the composition of the melts looks plausible: Along Join 3 in Fig. 10, the SiO_2 content of the melts decreases rapidly from left to right, i.e. the substitution $2Si^{4+} \rightleftarrows Zn^{2+}$, $2Al^{3+}$ is determining for the values of a_{hex}. The insertion of the larger (in comparison to Si^{4+}) cations Zn^{2+} and Al^{3+} clearly stretches the lattice in the a-direction. Join 1: The influence of the substitution $2Li^{+}$, $2Al^{3+} \rightleftarrows Zn^{2+}$, $2Al^{3+}$ is greater than that of the substitution $2Si^{4+} \rightleftarrows Zn^{2+}$, $2Al^{3+}$. While the overall concentration of larger cations does increase along Join 1 from left to right, the concentration of larger cations in the vacancies of the quartz structure decreases. The two competing effects lead to a smaller rise in the values of a_{hex} along Join 1 in the system $LiAlO_2$-$ZnAl_2O_4$-SiO_2. Along Join 2, the substitution $2Li^{+}$, $2Al^{3+} \rightleftarrows Zn^{2+}$, $2Al^{3+}$ becomes determining for the behavior of a_{hex}. In addition, the mol-% concentration of SiO_2 increases along Curve 2 in Fig. 10 from about 65 mol-% to 72 mol-%. This implies an increase in concentration of smaller cations in the quartz lattice, so that the decline in a_{hex} is understandable.

3.5.2. Expansion Properties of Crystallized Melts of the System $LiAlO_2$-$ZnAl_2O_4$-SiO_2

As can be seen from Fig. 11, two crystallization temperatures were chosen for the investigation of the expansion properties of crystallized melts in this system (Join 1 in Fig. 11). At 800°C, the metastable mixed crystals in this system could still be obtained without decomposition. Along Join 1b in Fig. 11, the α-values of melts crystallized at 800°C remained roughly constant at about α_{20-300} = $-17 \cdot 10^{-7}$/°C between 0 and 40% $ZnAl_2O_4$ by weight. At 900°C, crystallized samples on Join 3 likewise still showed no decomposition of the mixed crystals. Between 7 and 30% $ZnAl_2O_4$ by weight, the values of α_{20-300} remained constant at about $+5 \cdot 10^{-7}$/°C.
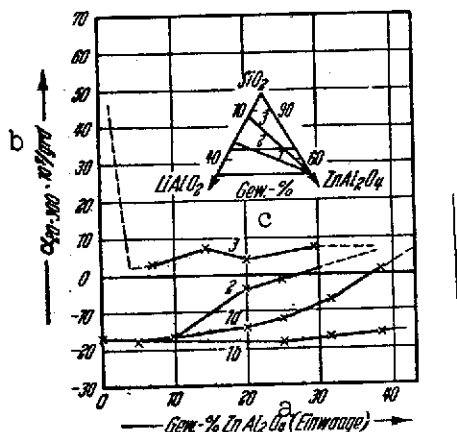
Fig. 11. Expansion properties of crystallized melts of the system SiO_2-$LiAlO_2$-$ZnAl_2O_4$. Crystallization temperatures: Join 1a, 2, 3: 900°C; Join 1b: 800°C.

Key: a. % $ZnAl_2O_4$ by weight (weighed sample)
b. Degree
c. % by weight

The lack of influence of $ZnAl_2O_4$ injection in mixed crystals with quartz structure of the system $LiAlO_2$-SiO_2 on the expansion values of the resulting mixed crystals in the range of concentrations investigated becomes intelligible if one recalls (Fig. 10) that the insertion /393 of $ZnAl_2O_4$ into mixed crystals of the system $LiAlO_2$-SiO_2 causes hardly any change in the lattice constants c_{hex}, whose magnitudes are indicative of the anisotropy of the expansion of the h-quartz lattice.

The rises in Curves 2 and 1a (Fig. 11), which show the expansion values as functions of the composition of crystallized melts of this system obtained at 900°C, can be attributed to a progressive (with increasing $ZnAl_2O_4$ content) decomposition of the mixed crystals into gahnite and mixed quartz crystals lower in $ZnAl_2O_4$. The growing Zn-spinel proportion in the crystalline phase distribution as the $ZnAl_2O_4$ content of the samples increases causes the rise in the α-values of the crystallized melts.

3.6. Metastable Mixed Crystals with Quartz Structure in the System $MgAl_2O_4$-$ZnAl_2O_4$-SiO_2

Even in this alkali-free pseudoternary system, we were able to obtain, at crystallization temperatures between 800 and

1000°C, metastable mixed crystals with quartz structure of the general form $Mg_{(1-x)}Zn_xO \cdot Al_2O_3 \cdot ySiO_2$ from glasses of the high-SiO_2 part of this system.

3.6.1. Lattice Constants of Metastable Mixed Quartz Crystals in the System $MgAl_2O_4-ZnAl_2O_4-SiO_2$

The behavior of the values of the hexagonal lattice constants of metastable mixed crystals in the high-SiO_2 part of the pseudoternary system and the position of the pseudobinary joins investigated can be read off of Fig. 12. The crystallization temperatures had to be varied between 800 and 1000°C, since there was no crystallization from high-SiO_2 melts at 800°C, while at temperatures over 800°C, melts high in $ZnAl_2O_4/MgAl_2O_4$ produced crystals which were already decomposing.
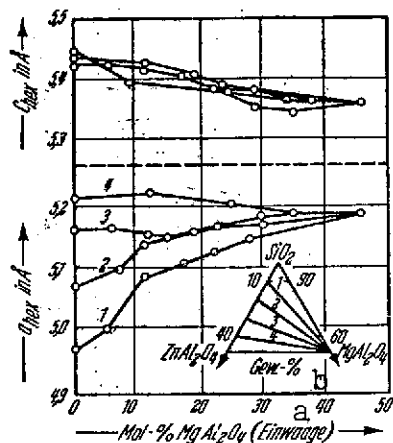

Fig. 12. Lattice constants of metastable mixed crystals with quartz structure in the system $SiO_2-ZnAl_2O_4-MgAl_2O_4$. Crystallization temperatures: Join 1: 1000°C; Joins 2,3: 900°C; Join 4: 800°C.

Key: a. Weighed sample
     b. % by weight

The values of C_{hex} for quartz mixed crystals in this system decrease uniformly with increasing $MgAl_2O_4$ content. This is in agreement with the results thus far described in the systems $MgAl_2O_4-SiO_2$ and $LiAlO_2-MgAl_2O_4-SiO_2$. The behavior of the lattice constants a_{hex} is also easy to see. Along Join 1 (from left to right), the substitution $2Si^{4+} \rightleftarrows Zn^{2+}, 2Al^{3+}$ is determining for the magnitude of a_{hex}. The more large cations (Al^{3+}, Zn^{2+}) enter the h-quartz lattice, the more the structure extends

24

in the a-direction. For mixed crystals on Joins 2 and 3 the influence of the $2Si^{4+} \rightleftharpoons (Mg,Zn)^{2+}, 2Al^{3+}$ substitution on the lattice constants a_{hex} is increasingly weakened by the effects of the substitution $Mg^{2+}, 2Al^{3+} \rightleftharpoons Zn^{2+}, 2Al^{3+}$. For the mixed crystals on Join 4 in Fig. 11, the a_{hex} curve tends to drop slightly. Obviously, the replacement of Zn^{2+} cations ($r_{Zn^{2+}}$ = = 0.83 Å) by Mg^{2+} cations ($r_{Mg^{2+}}$ = 0.78 Å) in the vacancies of the quartz structure causes a slight contraction of the lattice in the a-direction, due to the smaller ionic radius of Mg^{2+}.

3.6.2. Expansion Properties of Crystallized Melts of the System $MgAl_2O_4-ZnAl_2O_4-SiO_2$

A uniform crystallization temperature of 900°C was chosen for experiments to determine the expansion values of crystallized melts in this system. This did not produce the lowest possible α-values, since in the high-SiO_2 region inadequate crystallization, and in the high-$ZnAl_2O_4$ region incipient decomposition of the mixed crystals resulted in higher α-values. Accordingly, the α-values of the starting points of the curves 1, 2, 3 and 4 in Fig. 13 were relatively high. The lowest α-values obtainable in this system under crystallization conditions were $+10 \cdot 10^{-7}/°C$ in the vicinity of the composition (in wt-%): 70 SiO_2, 15 $MgAl_2O_4$, 15 $ZnAl_2O_4$. Additional $MgAl_2O_4$ caused the values to rise in line with the associated decrease in the lattice constants c_{hex}.

3.7. Metastable Mixed Crystals with Quartz Structure in the Pseudoquaternary System $MgAl_2O_4-ZnAl_2O_4-LiAlO_2-SiO_2$

Two joins were made through the pseudoquaternary system at 60 and 70% SiO_2 by weight. A number of specimens were studied in the described manner. Metastable mixed crystals with quartz structure were obtained either as the only phase detectable in
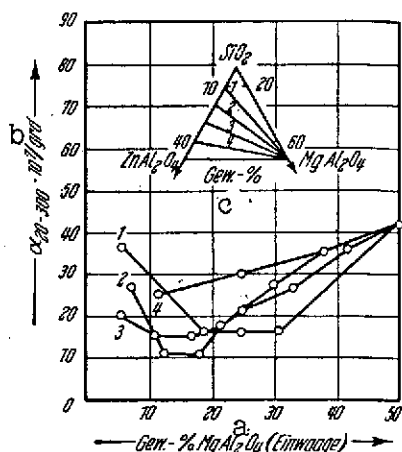
Fig. 13. Expansion properties of crystallized melts of the system SiO_2-$ZnAl_2O_4$-$MgAl_2O_4$. Crystallization temperature: 900°C.

Key: a. % $MgAl_2O_4$ by weight (weighed sample)
b. Degree
c. % by weight

x-ray crystallography, or else the principal devitrification phase. The specimens were tempered for 22 hours at 800 to 1000°C. The metastable mixed quartz crystals in this system have the general form

$$Li_{2-2(x+y)} \cdot Mg_x Zn_y \cdot O \cdot Al_2O_3 \cdot zSiO_2.$$

Mixed crystal formation in the pseudoquaternary region was again verified by lattice constant measurements. The results of investigations on some samples of the quaternary system with 60% SiO_2 by weight are summarized in Table 2 for selected examples. Tempering conditions, composition,

expansion values, and crystalline phase distribution of the tempered specimens are compared. A general tendency was observed: The expansion coefficients of the tempering products in the pseudoquaternary system, which contain metastable mixed crystals with quartz structure as the principal devitrification product, are greatly decreased by increasing insertion of $LiAlO_2$; the replacement of $Li_2Al_2O_4$ by $ZnAl_2O_4$ did not have any marked influence on the expansion properties of the resulting mixed crystals, while their α-values rose with increasing $MgAl_2O_4$ insertion (in line with the results of the studies on the pseudoternary system). Decreasing SiO_2 and increasing $ZnAl_2O_4$ concentrations in the mixed crystals enhance their tendency to decompose. The high α-values of the tempered samples in this system (e.g. Sample 14, Table 2) which were treated at 1000°C are very striking. Since the mixed quartz crystals still always constitute the principal devitrification product, the high α-values cannot be explained by the presence of the far smaller quantities of spinel and cristobalite.

26

TABLE 2. RESULTS OF THE STUDIES ON THE QUATERNARY SYSTEM WITH 60% SiO$_2$ BY WEIGHT.

Sample No.	Composition in wt-%*				Tempering temperature in °C (22 h)	α_{20-300} 10^7 deg.	Crystalline Phase Distribution
	SiO$_2$	LiAlO$_2$	MgAl$_2$O$_4$	ZnAl$_2$O$_4$			
1	60	8	12	20	800 900 1000	—1 10 75	Qu.-MK Qu.-MK, w Sp. Qu.-MK, Sp., Cr.
2	60	8	8	24	900 1000	5 78	Qu.-MK Qu.-MK, Sp., Cr.
3	60	8	4	28	800 900 1000	—3 0 99	Qu.-MK Qu.-MK Qu.-MK, Sp., Cr.
4	60	6	14	20	800 900 1000	31 12 70	Qu.-MK much Glass Qu.-MK Qu.-MK, Sp., Cr.
5	60	6	10	24	800 900 1000	10 4 54	Qu.-MK. Glass Qu.-MK Qu.-MK, Sp. w Cr.
6	60	6	6	28	800 900 1000	1 2 90	Qu.-MK Qu.-MK Qu.-MK, Sp., Cr.
7	60	6	2	32	800 900 1000	—6 —5 122	Qu.-MK + w Sp. Qu.-MK + w Sp. Qu.-MK, Sp., Cr.
8	60	4	16	20	900 1000	16 121	Qu.-MK Qu.-MK, Sp., Cr.
9	60	4	12	24	900 1000	3 130	Qu.-MK Qu.-MK, Sp., Cr.
10	60	4	8	28	800 900 1000	— 6 133	Qu.-MK Qu.-MK Qu.-MK, Sp., Cr.
11	60	4	4	32	800 900 1000	1 22 121	Qu.-MK Qu.-MK, w Sp. Qu.-MK, Sp.
12	60	2	18	20	800 900 1000	16 19 104	Qu.-MK, w Sp. Qu.-MK, w Sp. Qu.-MK, Sp. w Cr.
13	60	2	14	24	800 900 1000	11 14 123	Qu.-MK Qu.-MK, w Sp. Qu.-MK, Sp., Cr.
14	60	2	10	28	800 900 1000	7 12 153	Qu.-MK Qu.-MK, Sp. Qu.-MK, Sp., Cr.
15	60	2	6	32	800 900 1000	0 7 142	Qu.-MK Qu.-MK, w Sp. Qu.-MK, Sp., Cr.

*All samples contained an additional 2% TiO$_2$ and 2% ZrO$_2$ by weight.
Qu.-MK = Quartz mixed crystals; Sp. = spinel (Mg$_x$Zn$_y$)Al$_2$O$_4$; Cr. =
= cristobalite; w = little.

More precise x-ray crystallography showed that the mixed
crystals became so rich in SiO_2 through progressive decomposi-
tion (loss of $MgAl_2O_4/ZnAl_2O_4$) that they finally were present
at room temperature in their t-quartz modification, whose high
expansion values are known (see Section 3.1.3). Thus it is
possible through modified tempering programs to produce from
identical glass compositions crystalline products which differed
from one another by 140 α-units (see Table 2).

4. Summary of the Results

The questions posed at the beginning about the existence
region of metastable mixed crystals with quartz structure in
the pseudoquaternary system $LiAlO_2$-$MgAl_2O_4$-$ZnAl_2O_4$-SiO_2 and
about the influence of the compositions of the mixed phases on
their coefficients of expansion may be answered in summary:
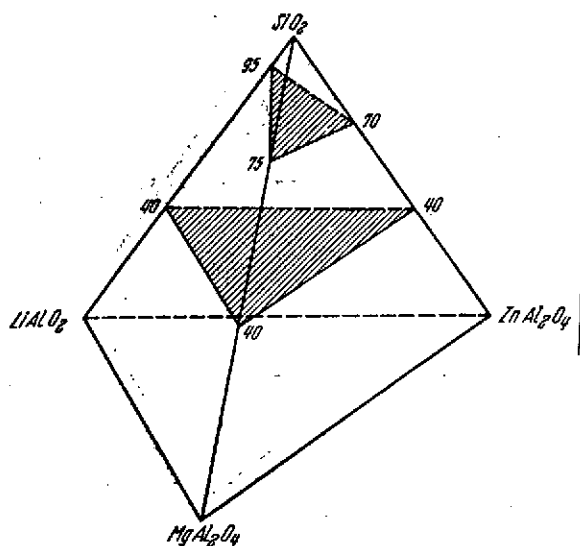Fig. 14 shows the space in the pseudoquaternary system within
which the metastable
quartz mixed crystals
can be obtained by
tempering for 22 hours
glasses which had
previously been
melted clear, and con-
tained 2% TiO_2 and 2%
ZrO_2 by weight, and
crystallizing them at
800 to 1000°C. While
a temperature of 900°C
was the most favorable
in the high-$LiAlO_2$ and
-$MgAl_2O_4$ region of the
existence range covered
in Fig. 14, a tempera-
ture of 800°C had to be

Fig. 14. Metastable mixed crystals
with quartz structure as the principal
product of devitrification in the system
SiO_2-$LiAlO_2$-$ZnAl_2O_4$-$MgAl_2O_4$. Crystal-
lization conditions: 22 hours, 800 to
1000°C.

chosen for cleanest possible crystallization of the mixed crystals in the high-$ZnAl_2O_4$ region, in order to prevent the decomposition of the mixed phases. With high-SiO_2 melts with high viscosities, the mixed crystals did not crystallize until temperatures around 1000°C were employed. The metastable mixed crystal formation in the system $LiAlO_2$-$MgAl_2O_4$-$ZnAl_2O_4$-SiO_2 was verified by measuring the lattice constants of the mixed crystals as functions of the composition of the melts from which they crystallized. Reproducing investigations in the system
$LiAlO_2$-SiO_2 proved that the metastable mixed crystals exhibit h-quartz structure up to a concentration of 80 mol-% SiO_2, but with higher SiO_2 concentrations had t-quartz structure at room temperature.

The elementary volume of the mixed crystals as a function of the composition of the glasses from which they crystallized was investigated in the systems $ZnAl_2O_4$-SiO_2, $LiAlO_2$-$MgAl_2O_4$-SiO_2, $LiAlO_2$-$ZnAl_2O_4$-SiO_2, and $MgAl_2O_4$-$ZnAl_2O_4$-SiO_2. With this information, it was possible to verify that mixed crystal formation in the indicated concentration region of the pseudoquaternary system $LiAlO_2$-$MgAl_2O_4$-$ZnAl_2O_4$-SiO_2 (Fig. 14) actually took place.

The polynary mixed crystals of this system contained in their quartz structures SiO_4 and AlO_4 tetrahedra, the ordering of which depends on the concentrations and the temperature history. The holes of the mixed crystal lattices can be occupied by adjacent Li^+, Mg^{2+}, and Zn^{2+} cations, and the previous statement applies to their ordering as well.

The α-values of the polynary mixed crystals decrease as the Li^+ and Zn^{2+} concentrations grow, and increase as the Mg^{2+} concentration grows. Under the given crystallization conditions, the less SiO_2 and the more $ZnAl_2O_4$ the mixed crystals contain, the greater their tendency to decompose.

The possibility of the substitutions $2Si^{4+} \rightleftarrows$ (Ni, Mn, Cu, Co)$^{2+}$ $2Al^{3+}$ in the h-quartz lattice of the metastable mixed crystals is still being investigated at present.

The results presented have defined the boundaries of the concentration range in the base system Li_2O-MgO-ZnO-Al_2O_3-SiO_2 within which it is possible to obtain crystalline phases with low coefficients of thermal expansion -- information which is important in the development of glass-ceramic materials with high resistance to temperature changes.

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/396

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